42. Organic Phosphorus Compounds 59[1]) A New Method for the Synthesis of Phosphonic Dichlorides [1]

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Summary. Heating of thiophosphonic dichlorides, $RP(S)Cl_2$, $R = CH_3, C_2H_5, C_6H_5$, with a molar equivalent of $SOCl_2$ under pressure at 150° for 5 to 8 h yields phosphonic dichlorides in quantitative yield. In addition sulfur and sulfur dichloride is formed according to the equation:

$$RP(S)Cl_2 + SOCl_2 \rightarrow RP(O)Cl_2 + SCl_2 + S$$

This method is particularly useful for the preparation of $CH_3P(O)Cl_2$ since it was observed that chlorination of $CH_3P(O)(OCH_3)_2$ with PCl_5 yields $CH_3OP(O)Cl_2$ as a by-product which is difficult to separate from $CH_3P(O)Cl_2$. On the other hand chlorination of methylphosphonic acid with PCl_5 also gives pure $CH_3P(O)Cl_2$.

$$CH_3P(O)(OH)_2 + 2\,PCl_5 \rightarrow CH_3P(O)Cl_2 + 2\,HCl + 2\,POCl_3$$

Several methods have been described in the literature for the preparation of phosphonic dichlorides [2]. One of the most widely used procedure consists in the conversion of phosphonates to phosphonic dichlorides by reaction with PCl_5 [2]. This reaction is, however, not as clean as given in the equation:

$$RP(O)(OR')_2 + PCl_5 \rightarrow RP(O)Cl_2 + 2\,POCl_3 + 2\,R'Cl$$

Often considerable amounts of ester-chlorides, RP(O)Cl(OR) [3] and other compounds are formed which are difficult to separate from the dichlorides. For example, we observed that when dimethyl-methylphosphonate, $CH_3P(O)(OCH_3)_2$ was treated with PCl_5 using $POCl_3$ as solvent, considerable amounts of $CH_3OP(O)Cl_2$ were formed as by-products which could not be separated by fractional distillation from $CH_3P(O)Cl_2$.

$$CH_3P(O)(OCH_3)_2 + POCl_3 \rightarrow CH_3P(O)(OCH_3)Cl + CH_3OP(O)Cl_2$$

We therefore hydrolyzed the phosphonates first to the acid and then chlorinated the acids with PCl_5 to the dichlorides as described in the literature [4]. In this way pure $CH_3P(O)Cl_2$ was obtained.

$$CH_3P(O)(OCH_3)_2 + 2\,HCl \rightarrow 2\,CH_3Cl + CH_3P(O)(OH)_2 \xrightarrow{2\,PCl_5} CH_3P(O)Cl_2 + 2\,HCl + 2\,POCl_3$$

Similarly, $C_2H_5P(O)Cl_2$ was also prepared in this way.

This procedure is, however, somewhat lengthy and troublesome and therefore a simpler method was sought.

Recently, methyl and ethyl-thiophosphonic dichlorides became commercially available[2]). Therefore attempts were made to convert these thiophosphonic dichlorides in one step to phosphonic chlorides.

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[1]) Part 58, see [1].

[2]) *Ethyl Corporation*, Baton Rouge, La.

It is known from the literature [5] [6] that thiophosphinic chlorides may be converted to phosphinic chlorides by reaction with thionyl chloride at reflux temperature (80°). The method was, however, less successful in converting thiophosphonic dichlorides to the corresponding phosphonic dichlorides. Thus heating of $PhP(S)Cl_2$ with

$$R_2P(S)Cl + SOCl_2 \rightarrow R_2P(O)Cl + SCl_2 + S$$

$SOCl_2$ for 2 h to 80° (reflux) effected no reaction [6]. Also heating of $PSCl_3$ with $SOCl_2$ for 10 h to 80° caused no reaction. And on heating of $PhP(S)Cl_2$ with $SOCl_2$ for 10 h to 80° only at 24% conversion to $PhP(O)Cl_2$ was achieved [6]. We observed that $CH_3P(S)Cl_2$ remained unchanged when it was heated with $SOCl_2$ for 8 h to 80°.

It has now been found that heating of thiophosphonic dichlorides with $SOCl_2$ to 150° for 5 to 8 h under pressure effects a 100% conversion to the corresponding phosphonic dichlorides. In addition sulfur and sulfur dichloride is formed according to the equation:

$$RP(S)Cl_2 + SOCl_2 \rightarrow RP(O)Cl_2 + SCl_2 + S$$

Thus when a 1:1.2 mixture of $CH_3P(S)Cl_2$ and $SOCl_2$ was heated in a bomb tube to 150° for 2 h, a product was obtained which consisted of 92 mol-% $CH_3P(O)Cl_2$ and 8 mol-% $CH_3P(S)Cl_2$; further heating for 3 h at 150° changed the composition to 98.5 mol-% $CH_3P(O)Cl_2$ and 1.5 mol-% $CH_3P(S)Cl_2$; and finally heating for another 3 h effected a 100% conversion to $CH_3P(O)Cl_2$.

This reaction seems to be general. When $C_2H_5P(S)Cl_2$ and $PhP(S)Cl_2$ were heated with $SOCl_2$ in a bomb tube to 150° for 5 to 8 h a 100% conversion to the corresponding phosphonic dichlorides was observed.

Experimental. – 1. *$CH_3P(O)(OCH_3)_2(I)$ and $PCl_5 \rightarrow CH_3P(O)Cl_2(II)$.* $CH_3P(O)(OCH_3)_2$ was obtained in 85.3% yield from $(CH_3O)_3P$ and a catalytic amount of NaI according to the literature [7], b.p. 70°/11 torr. ^{1}H-NMR. (in CCl_4): PCH_3 1.33 ppm (*d*, J_{PCH} 17.7 Hz, 3H), OCH_3 3.62 ppm (*d*, J_{POCH} 11 Hz, 6H); ^{31}P- 31.5 ppm (in CCl_4) (Lit. [8] – 32.4 ppm).

A mixture of 116 g (0.93 mol) of $CH_3P(O)(OCH_3)_2$ in 120 ml $POCl_3$ and 131 g (0.955 mol) of PCl_3 was treated with Cl_2 and then heated to 80–90° as described in the literature [4, p. 388]. Distillation gave a product which contained

$CH_3P(O)Cl_2$:	^{31}P- 44.5 ppm; ^{1}H (in CCl_4): 2.48 ppm (*J* 16.5). Lit. [9] 2.57 ppm (*J* 16.1);
$CH_3P(O)Cl(OCH_3)$:	^{31}P- 31 ppm; ^{1}H: PCH_3 1.90 ppm (*J* 17.5); OCH_3 3.80 ppm (*J* 13.4). Lit. [9] PCH_3 2.03 ppm (*J* 17.4); OCH_3 3.82 ppm (*J* 13.4);
$(CH_3O)_2P(O)Cl$:	^{31}P- 6.5 ppm; ^{1}H: 3.85 ppm (*J* 13.5). Lit. [9] 3.87 ppm (*J* 13.4);
$CH_3OP(O)Cl_2$:	^{31}P- 4.5 ppm; ^{1}H 4.0 ppm (*J* 16.4). Lit. [9] [10] 4.02 ppm (*J* 17.1).

Therefore the mixture was treated again with PCl_5 and heated for 2 h to 80°. Fractional distillation gave now a product, b.p. 47.5–50°/10 Torr (84.2 g) which consisted of 75.4 mol-% $CH_3P(O)Cl_2$ (^{1}H (in CCl_4): 2.45 ppm (J_{PCH} 17 Hz) and 24.6 mol-% $CH_3OP(O)Cl_2$ (^{1}H (in CCl_4): 3.98 ppm, J_{POCH} 16.5 Hz) (Lit. [10] 4.08 ppm (in $CHCl_3$), J_{POCH} 16.7 Hz). On standing $CH_3P(O)Cl_2$ crystallized out. It was filtered off and found to be pure, m.p. 32°.

2. *$CH_3P(O)(OH)_2(III)$ and $PCl_5 \rightarrow CH_3P(O)Cl_2(II)$.* Hydrolysis of I with conc. HCl at reflux for 14 h gave III in quantitative yield, eq. weight found: 100.12, calc. 96.02. Treatment of 80 g (0.83 mol) III with 430 g (2.07 mol) PCl_5 first at 65–75° then 9 h reflux gave on fractional distillation 238.5 g $POCl_3$ and 81.2 g (73.5%) $CH_3P(O)Cl_2$, b.p. 34–48°/10 Torr which crystallized on standing to the greater part. ^{1}H-NMR. (in CCl_4) indicated that the product is pure II: CH_3 at 2.47 ppm (J_{PCH} 16.7 Hz); ^{31}P- 44.5 ppm (Lit. [8] ^{31}P- 44.5 ppm).

3. *$C_2H_5P(O)(OH)_2(IV)$ and $SOCl_2 \rightarrow C_2H_5P(O)Cl_2$ (V).* $EtP(O)(OEt)_2$ was prepared from $(EtO)_3P$ and NaI [4], b.p. 75–77°/11 Torr; ^{1}H-NMR. (in CCl_4): a) CH_3 1.28 ppm (*t*); b) PCH_2 0.94–1.95 ppm (*m*), a+b 10.9 H; OCH_2 4.0 ppm (J_{HH} 7, J_{POCH} 8.5 Hz, 4.06 H); ^{31}P- 32 ppm (neat).

Hydrolysis of ethylphosphonate with a 40% solution of HBr gave a quantitative yield of IV as an oily, viscous liquid. Treatment of 79.5 g (0.723 mol) IV with 190 g (1.53 mol) $SOCl_2$ at 70° for 3 h, then at 105° until evolution of HCl ceased, gave on distillation 55.5 g (52.8%) V, b.p. 60–61°/10 Torr; ^{1}H-NMR. (in CCl_4): CH_3 at 1.38 ppm (2 *t*, J_{HH} 7, J_{PCCH} 30 Hz, 2.99 H); CH_2 at 2.58 ppm (2 *qu*, J_{HH} 7, J_{PCH} 16 Hz, 2.01 H); ^{31}P- 53.5 ppm (neat) (Lit. [8] ^{31}P- 53 ppm).

4. *$CH_3P(S)Cl_2$ and $SOCl_2$ at 80°.* A mixture of 14.9 g (0.1 mol) $CH_3P(S)Cl_2$ and 1.46 g (0.12 mol) $SOCl_2$ was refluxed for 8 h at 80°. ^{1}H- and ^{31}P-NMR. indicated that after this period no reaction had occurred. $CH_3P(S)Cl_2$ was quantitatively recovered by distillation, b.p. 39–43°/0.1 Torr, n_D^{20} 1.5470; ^{1}H (in $CHCl_3$): CH_3 at 2.78 ppm (J_{PCH} 14.5 Hz) (Lit. [11] 2.88 (J 14.6 Hz); ^{31}P -79.5 ppm (neat) (Lit. [8] ^{31}P- 79.4 ppm).

5. *$CH_3P(S)Cl_2$ and $SOCl_2$ at 150°.* Three bomb-tubes were filled each with 10 g (0.067 mol) of $CH_3P(S)Cl_2$ and 9.5 g (0.08 mol) of $SOCl_2$ and heated in a bomboven to 150°. Tube 1 was removed after 2 h at 150°. ^{1}H- and ^{31}P-NMR.-analysis indicated that its content consisted of 92 mol-% $CH_3P(O)Cl_2$ [^{1}H-NMR. (in $CDCl_3$): CH_3 at 2.28 ppm (J_{PCH} 16.4 Hz), ^{31}P- 44 ppm] and 8 mol-% $CH_3P(S)Cl_2$ [^{1}H-NMR. (in $CDCl_3$): CH_3 at 2.78 ppm (J_{PCH} 14.8 Hz) ^{31}P- 80 ppm].

In addition a trace of $POCl_3$ was seen in the ^{31}P-NMR. at -3.5 ppm.

Tube 2 was removed after 5 h at 150°. ^{1}H- and ^{31}P-NMR. analysis indicated that the solution consisted of 98.6 mol-% $CH_3P(O)Cl_2$ and 1.4 mol-% $CH_3P(S)Cl_2$.

Tube 3 was removed after 8 h at 150°. ^{1}H- and ^{31}P-NMR.-analysis indicated that the solution consisted of a 100 mol-% $CH_3P(O)Cl_2$. Distillation of the contents of each tube gave $CH_3P(O)Cl_2$ b.p. 53–54°/10 Torr, m.p. 30–32° and SCl_2; in addition crystalline sulfur was isolated.

6. *$C_2H_5\overset{\overset{S}{\|}}{P}Cl_2 + SOCl_2$ at 150°.* A bomb tube was filled with 20 g of $C_2H_5P(S)Cl_2$ (0.123 mol) and 17.6 g (0.148 mol) of $SOCl_2$ and heated for 5 h to 150°. After this period a dark violet solution was present and crystalline sulfur had precipitated. ^{1}H- and ^{31}P-NMR.-analysis indicated that $C_2H_5P(O)Cl_2$ was formed in a 100% conversion. Distillation gave pure $C_2H_5P(O)Cl_2$ b.p. 33°/3 Torr, 75–78°/50 Torr. ^{1}H-NMR. (in $CDCl_3$): CH_3 at 1.4 ppm (2 *t*, J_{HH} 7.5, J_{PCH} 30 Hz, 3H); CH_2 at 2.5 ppm (2 *qu*, J_{HH} 7.5, J_{PCCH} 14.5 Hz, 2H), ^{31}P- 54 ppm (neat); contains a trace of $P(O)Cl_3$ at -3.5 ppm (must have been formed by a P—C bond cleavage.)

7. *$C_6H_5\overset{\overset{S}{\|}}{P}Cl_2 + SOCl_2$ at 150°.* A bomb tube was filled with 20 g (0.095 mol) $PhP(S)Cl_2$ and 13.6 g (0.114 mol) $SOCl_2$ and heated in a bomb oven to 150° for 5 h. A yellow solution is obtained which consist, according to ^{1}H- and ^{31}P-NMR.-analysis, of 82 mol-% $PhP(O)Cl_2$ (^{31}P- 34 ppm) and 18 mol-% $PhP(S)Cl_2$ (^{31}P- 74.5 ppm) (Lit. [8] -34 ppm and -74.8 ppm, respectively).

Another tube filled with the same amounts of reagents was heated for 8 h to 150°. Thereby a quantitative conversion to $PhP(O)Cl_2$ was effected. Distillation gave SCl_2 and $PhP(O)Cl_2$, b.p. 104°/4 Torr; ^{31}P- 34 ppm (neat); ^{1}H-NMR. (in $CDCl_3$): *m*- and *p*-CH 7.65 (*m*, 3H); *o*-CH 8.06 (*m*, 2H).

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